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Polyethylene glycol assisted micellar, interfacial and phase separation studies of triblock copolymer–nonionic surfactant mixtures

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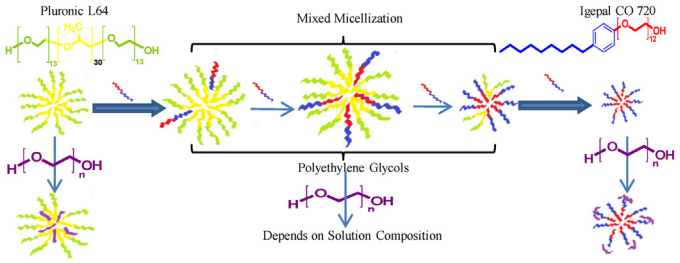
HIGHLIGHTS

- Pluronic L64–Igepal CO720 mixtures studied in presence of Polyethylene glycols.
- The micellization in mixtures is seen to be composition dependent.
- Variation in behavior of polyethylene glycols with its molecular weight.
- Mixtures of Igepal CO 720/Pluronic L64/PEGs act as surface tension reducers.

GRAPHICAL ABSTRACT



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ABSTRACT

Owing to the relevancy of surfactant–polymer mixtures in several industrial and technological applications, the present work aims to study the aqueous triblock copolymer, Pluronic L64 – nonionic surfactant, Igepal CO 720 mixtures in the presence of various polyethylene glycols viz. PEG 15000, PEG 6000, PEG 2000 and PEG 600. This has been evaluated in terms of micellar, interfacial and phase separation behavior using fluorescence spectroscopy, surface tension, cloud point and dynamic light scattering measurements. The behavior of mixed micelles is seen to be dependent on the solution composition. Increasing the concentrations of Igepal CO 720 in mixtures, the mixed micelles shift from being Pluronic L64 rich to Igepal CO 720 dominated ones. An insight in the behavior of mixtures using PEGs exemplifies this dominance of Igepal CO 720 in the mixed micelles. Results indicate that both the micellization and clouding tendencies of Pluronic L64 are facilitated by the presence of all types of PEGs. However in Igepal CO 720, the micellization gets retarded while clouding behavior is a function of the molecular weight of PEGs. The hydrodynamic diameter of micellar aggregates of pure Pluronic L64, Igepal CO 720 as well as their mixtures is found to increase in the presence of PEGs.

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1. Introduction

Surfactants are ubiquitous materials, epitomizing their presence from common household items to complex industrial processes. Among various classes of surfactants, a versatile category constituted by triblock copolymers or Pluronics, belonging to nonionic surfactants is being highly investigated because of their uniqueness in exhibiting concentration/temperature dependent micellization, anomalous turbidity at certain concentration/temperature, solubilization at concentrations below the critical micellar concentration and the reversible thermo rheological behavior [1] in comparison to conventional nonionic surfactants. These triblock copolymers are made up of polyethylene oxide (PEO) and polypropylene oxide (PPO) blocks and generally represented as $(EO)_n$–$(PO)_m$–$(EO)_n$.

As the triblock copolymers are making their way ahead in diverse fields as templating agents for the preparation of thin films of mesoporous metal oxide [2,3], in the separation of DNA and proteins [4,5], as nanoreactors [6–8], etc., the researchers are turning their attention to the complex systems of triblock

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copolymers with other components such as inorganic salts [9], organic additives [10,11] and other surfactants. Mixtures of triblock copolymers with surfactants of various types generally offer improved performance characteristics, better colloidal stability, finely tuned medium viscosity and superior rheological personality. In this regard, numerous investigations including ours [12–14] have been carried to evaluate various triblock copolymer–ionic surfactant mixtures viz., P103/F108 with gemini surfactants [15], F88/P105 with CTAB [16], P105 with SDS/DTAB/TX-100 [17] and P123/F127 with SDS/HTAB [18], etc. Schillen and co-workers [18] have reported the hindrance of micelle formation in triblock copolymers in the presence of SDS and the formation of two types of copolymer-surfactant complexes is illustrated but Ganguly et al. [19] have pointed out the existence of only one type of micellar aggregates. However, a very few studies address the issue of triblock copolymer–nonionic surfactant mixtures [20,21] and that too concerning the morphological characterization of these mixtures using techniques such as DLS/SANS/Cryo-TEM. To this end, we have chosen to characterize the aqueous binary mixtures of triblock copolymer, Pluronic L64 and nonionic surfactant, Igepal CO 720 using fluorescence, surface tension, cloud point and dynamic light scattering (DLS) measurements. Pluronic L64 is a triblock copolymer with the formula $(EO)_{13}$–$(PO)_{30}$–$(EO)_{13}$ whose micellar structure consists of a core made up of hydrophobic PPO segments and a shell formed from hydrophilic PEO units. Igepal CO 720 belongs to polyoxyethylene surfactants having a nonyl chain attached to phenyl moiety as their hydrophobic tail and a chain of twelve ethylene oxide units as hydrophilic head group. In spite of being nontoxic and having a wide applicability [22,23], Igepal CO 720 has been least investigated and this formed the basis of our interest in this compound.

As additives are known to alter the physiochemical properties (critical micellar concentration, micellar size and phase behavior) of the surfactant solutions through modification of the surfactant–solvent interactions [24], we extended our studies further to check the effect of polyethylene glycols of varying molecular mass (PEG 15000, PEG 6000, PEG 2000 and PEG 600) on the aqueous mixtures of Pluronic L64 and Igepal CO 720. The reason for the employment of PEGs as additives in our study lies in their low cost, easy availability, non-volatility, biodegradability [25] and above all a wide applicability of the surfactant–polymer mixtures involving nonionic surfactants as detergents, emulsifiers, wetting or foaming agents and the polymers to control the viscosity of solutions. For this, firstly the interactions of various PEGs were examined with each of Pluronic L64 and Igepal CO 720. This endowed us with an idea that Pluronic L64 and Igepal CO 720, belonging to two different categories of nonionic surfactants, behave differently in the presence of PEGs and hence advantage was taken of this fact to characterize the Pluronic L64 + Igepal CO 720 mixtures using PEGs. In the work presented here, we have tried to analyze our results in terms of critical micellar concentration (*cmc*), interfacial parameters like surface excess (Γ_{max}), minimum area per molecule (A_{min}), surface pressure (π_{cmc}), hydrodynamic diameter (D_h) and the thermodynamic appraisal in terms of energetics of clouding (ΔG_c°, ΔH_c° and $T\Delta S_c^\circ$), and standard free energies of micellization (ΔG_m°) and adsorption (ΔG_{ads}°).

2. Experimental

2.1. Materials

Pluronic L64 and Igepal CO 720 were obtained from Sigma Aldrich. Polyethylene glycols (PEG 15000, PEG 6000, PEG 2000 and PEG 600) were all Spectrochem, India products. All chemicals were used as received and were of analytical grade. An analytical balance (Sartorius analytic) with a precision of ±0.0001 g was used for weighing the amount of different substances. The solutions were prepared by dissolving accurately weighed quantities in requisite volumes of deionised double distilled water.

2.2. Methods

2.2.1. Fluorescence measurements

The steady state fluorescence measurements of various single surfactants (Pluronic L64 and Igepal CO 720) and mixed surfactant systems (Pluronic L64 + Igepal CO 720) with and without polyethylene glycols (PEG 15000, PEG 6000, PEG 2000 and PEG 600) were performed on a Varian Cary Eclipse Fluorescence spectrophotometer using a 10 mm path length quartz cuvette at 298.15 ± 0.1 K. The concentration of pyrene used in all the measurements was approximately equal to 10^{-6} mol dm^{-3}. The ratio of the intensity of pyrene emission, i.e. I_1/I_3 at 373 and 384 nm, respectively, was used for evaluating the polarity of the environment in which the pyrene was solubilized.

2.2.2. Surface tension measurements

The surface tension values were measured using a Du Nouy ring Tensiometer (Kruss Easy Dyne tensiometer) from Kruss Gmbh (Hamburg, Germany) equipped with thermostat, using a platinum ring at 298.15 ± 0.5 K. Concentrated stock solutions of surfactant + additives were prepared in deionised double distilled water and successive additions were made of these stock solutions to additives + water systems to obtain the measurements. All measurements were performed after giving overnight time for stabilization. The accuracy in the measurement of surface tension with tensiometer is ±0.15 mN m^{-1}.

2.2.3. Cloud point measurements

The cloud point (CP) for the various systems mentioned above was determined by heating them in glass tubes suspended in an oil bath, whose temperature was increased gradually with constant stirring at a rate of about 0.1 K min^{-1}. CP was determined visually by noting the abrupt change in the appearance of surfactant solution from clear to turbid. The temperature at which turbidity first appeared was recorded. The solution was then allowed to cool slowly, and the temperature at which it became clear again was also recorded. The results obtained from the two steps agreed within ± 0.5 K. The mean of the two temperatures was taken as the cloud point.

2.2.4. Dynamic light scattering (DLS) measurements

The DLS measurements were performed using a Malvern 4800 Autosizer employing 7132 digital correlator and an argon ion laser at 514.5 nm as the light source with a maximum output power of 2 W. The samples of micellar solutions were properly filtered to avoid interference from dust particles. The scattered intensity for the various systems under study was obtained at an angle of 120° to the incident beam and data was collected at least five times for 30 s for each independent sample. The corresponding hydrodynamic diameters (D_h) were calculated using the Stoke–Einstein relationship as per equation (1).

$$D = \frac{k_B T}{3\pi\eta D_h} \quad (1)$$

where D is the diffusion coefficient, k_B is Boltzmann constant, T is the sample temperature in Kelvin, η is viscosity of the solvent and D_h is the hydrodynamic diameter of the aggregate.

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